ANHARMONIC VIBRATIONAL PROPERTIES OF MOLYBDENUM SULPHIDES FROM MACHINE-LEARNING DRIVEN CANONICAL SPACE SAMPLING

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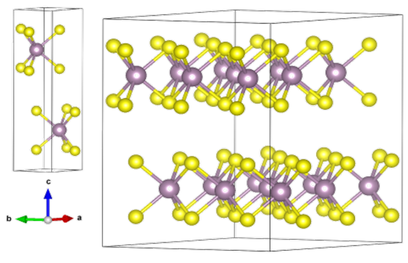
INTRODUCTION

Molybdenum Sulphides:
- non-toxic, inexpensive, eco-friendly;
- good catalysts for the **Hydrogen Evolution Reaction** (HER).

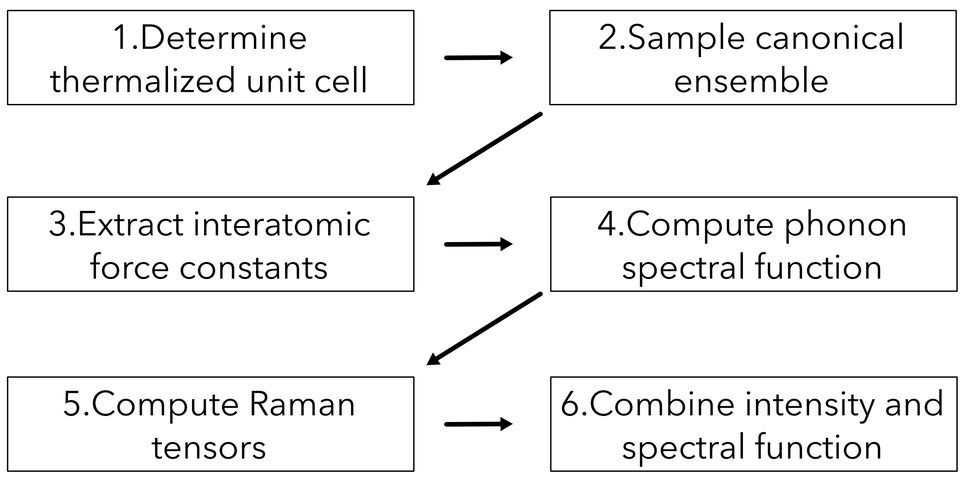


No structure[1] ⟶ no mechanism

Vibrational spectroscopy can unveil **local structural features**.

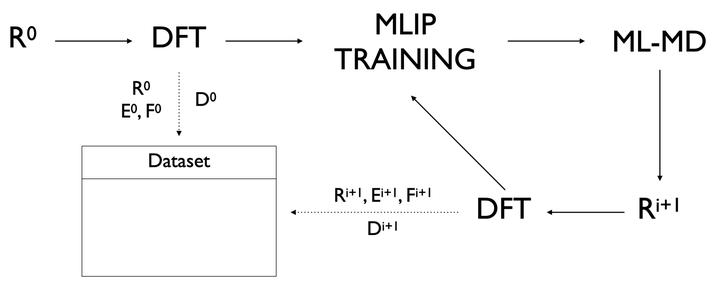
We investigate the temperature-dependent vibrational properties of MoS_2, such as phonons and **Raman** activity, by combining state-of-the-art **Machine Learning-Interatomic Potentials** (MTP model[2]) with **Molecular-Dynamics** simulations.

THE WORKFLOW



THE TRAINING DATASET

The training dataset for the MLIP was generated using the **Machine Learning Assisted Canonical Sampling** (MLACS) algorithm[4]. It consists of a self consistent iterative scheme of **short MLMD sampling** using an MLIP which is **retrained** on the fly at each augmentation of the dataset, until error convergence.



CONCLUSION

- The **MTP model** yields **good accuracy** in energy, forces and stress prediction, ensuring **reliable MLMD**.
- The **TDEP method** leads to very good results, in **agreement with experiments**.
- Further investigation is needed to attain a better description of the Raman peak intensities vs. temperature.

REFERENCES

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[2] Ivan S. Novikov et al., Machine Learning: Science and Technology, 2 (2020)

[3] Olle Hellman et al., Physical Review B, 10 (2013) 104111.

[4] Aloïs Castellano et al., Physical Review B, 16 (2020) L161110

[5] Tsachi Livneh and Eran Strer, Physical Review A, 19 (2010) 195209

[6] Satyaprakash Sahoo et al., The Journal of Physical Chemistry C, 17 (2013) 9042-9047

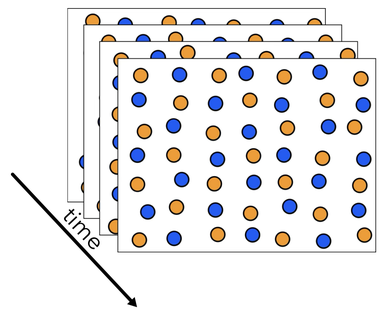
TEMPERATURE DEPENDENT EFFECTIVE POTENTIAL[3]

Describe the potential energy surface with the best n-order polynomial of the atomic displacements around the equilibrium geometry.

$$U(\{\mathbf{u}_i\}) \approx U(0) + \sum_i \underbrace{\left.\frac{\partial U}{\partial \mathbf{u}_i}\right|_{eq}}_{=0} \mathbf{u}_i + \sum_i \underbrace{\left[\sum_j \Phi^{(2)}_{ij}\mathbf{u}_j\right]}_{\mathbf{F}^{(2)}_i} \mathbf{u}_i + \sum_i \underbrace{\left[\sum_{j,k} \Phi^{(3)}_{ijk}\mathbf{u}_j\mathbf{u}_k\right]}_{\mathbf{F}^{(3)}_i} \mathbf{u}_i$$

The set of parameters $\{\Phi^{(2)}_{ij}\}$and $\{\Phi^{(3)}_{ijk}\}$are the 2nd and 3rd-order interatomic force constants and also the parameters of the model; they are physical quantities related respectively to the **phonon frequencies** and the **phonon lifetimes**.

Goal: optimize the parameters to describe the vibrational dynamics of the system **at a finite temperature**.
- Sample the canonical ensamble (trough MD) of the **thermalised unitcell**.
- Minimize the model error on the atomic forces with respect to the reference.



$$\Delta\mathbf{F} = \frac{1}{N_t}\sum_{i,t}\left|\mathbf{F}^{\mathrm{MD}}_{i,t} - \mathbf{F}^{\Phi}_i\right|^2$$

$$\{\Phi^{(2)}_{ij}\},\{\Phi^{(3)}_{ijk}\} = argmin\left\{\Delta\mathbf{F}\left(\{\Phi^{(2)}_{ij}\},\{\Phi^{(3)}_{ijk}\}\right)\right\}$$

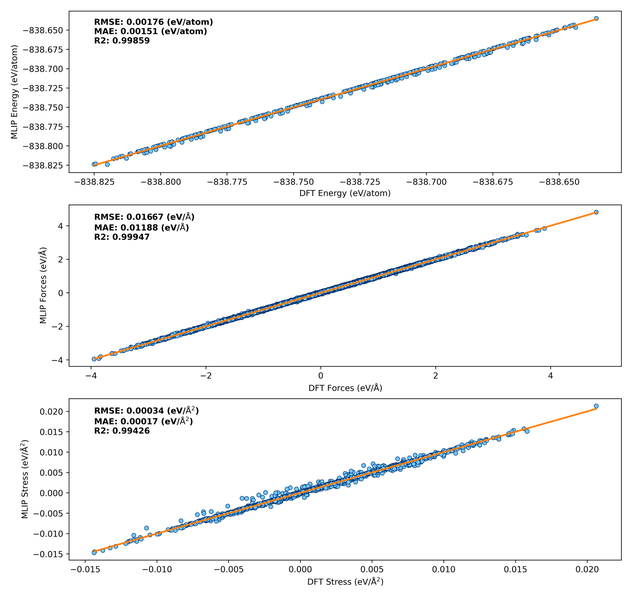
Note that the canonical sampling accounts for the **temperature dependence** and the **anharmonicity** of the system. We perform the sampling via NVT **Machine Learning-Molecular Dynamics** (MLMD) simulations employing **Machine Learning Interatomic Potentials** (MLIPs) as force fields instead of the less accurate classical ones.

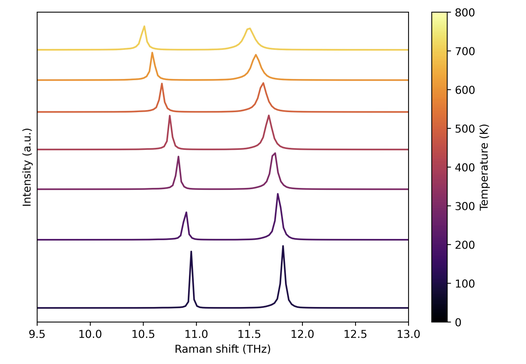
THE RAMAN SPECTRUM

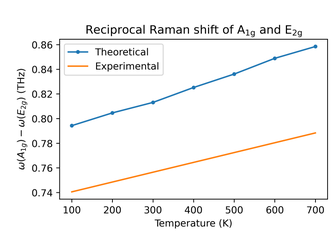
- Displace the unit cell according to each mode and compute the **dielectric tensor**.
- Compute Raman tensor and **Raman intensity**.
- Combine intensity with **spectral function**.

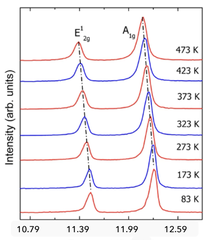
$$\alpha_m = \frac{\partial\chi}{\partial|u_m|} \approx \frac{\chi(|u_m^+|) - \chi(|u_m^-|)}{|u_m^+| - |u_m^-|} \longrightarrow I_m = |\mathbf{e}_i \cdot \alpha_m \cdot \mathbf{e}_o|^2 \longrightarrow S(\omega) = \sum_m J_m(\omega)\cdot I_m$$

RESULTS









The spectra we obtained are in good agreement with experiments[5,6]. The major discrepancy is in the relative intensity vs. T of the two peaks, which is under investigation.

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